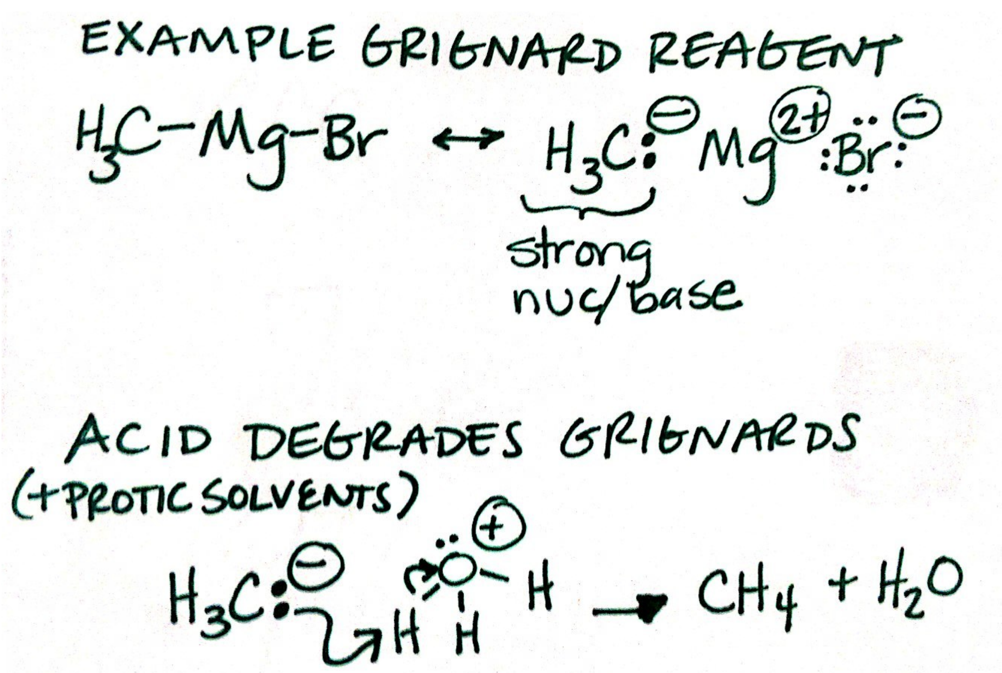
12AL Experiment : "Pseudo" Grignard Reaction

Safety: Proper lab goggles/glasses must be worn (even over prescription glasses). As always, ask where organic waste containers are located in the lab.

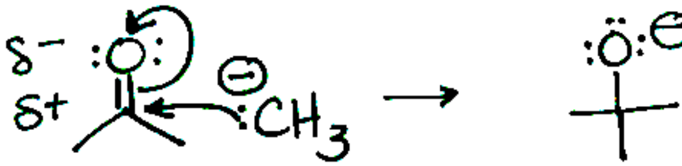
Background:

Grignard reactions are very useful reactions in organic syntheses because you are able to create new C-C bonds and extend your carbon chain. They are relatively simple nucleophilic reactions to perform, although the classic Grignard reaction is a bit difficult to control.

The classic Grignard reagent is prepared by reacting Magnesium metal with an alkyl halide to form a carbanion nucleophile. This highly reactive nucleophile can then attack an electrophilic center. However, magnesium Grignard reagents cannot be used in polar protic environments, like water, because they react vigorously with the acidic hydrogen atoms. This limits the number of experiments that can be run easily with magnesium based grignards; afterall, the atmosphere contains water vapor and so a "dry" environment is difficult to obtain. Please bear in mind that water is often used to "quench" Grignard reactions after they are completed – degrade any leftover Grignard reagent and to protonate any anions.



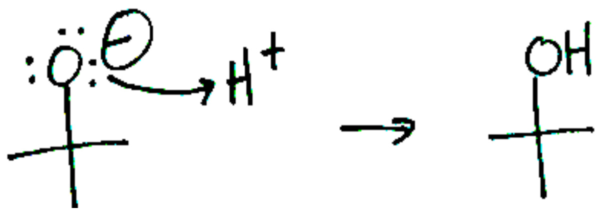
*RXN WITH A GRIGNARD



① basic environment

*GRIGNARDS ATTACK ANY δ+ SITE; DOES NOT HAVE TO BE C=O

② if you want to protonate oxide ion and degrade leftover grignard, add acid after rxn.



"Pseudo" Grignard reagents are prepared using other metals like zinc – still reactive enough to produce a carbanion nucleophile when the zinc reacts with the alkyl halide, but not strong enough to react with a polar protic environment. Thus, we are able to run a Grignard reaction in an aqueous environment today without worry of any violent reactions – however, safety should always be on your mind!
(Adapted from Moorpark College)

Objective: To successfully react benzaldehyde with 1-bromo-2-propene (allyl bromide). To understand the mechanism of Grignard and Pseudo-Grignard Reactions in order to predict products.

Procedure:

1. Combine 0.320 grams of powdered Zinc and 4.0 mL of saturated aqueous ammonium chloride into a 25 mL Erlenmeyer flask. Add a stir bar. Obtain a stir plate. (*You will not being using the heat! Only the stirring.)

2. In a 10 mL beaker in the HOOD, use your micro-syringe to measure out 0.20 mL of benzaldehyde and combine with 2.0 mL of THF.

3. Pour the benzaldehyde/THF solution gently into the Erlenmeyer flask mixture from step 1. Let the mixture stir for 10 min.

4. Using your CLEANED syringe, measure out 0.40 mL of allyl bromide and add it to your mixture. You should see evidence of a reaction immediately. Let the mixture stir for 45 min (no heat).

5. After stirring for 45 min, add 3 mL of ether, stir briefly, then filter the reaction mixture using your securely clamped micro-filtration set-up. Pour another 2 mL of ether over the solid precipitate to thoroughly wash it in order to get all your synthesized product into the liquid in the filtering flask.

6. Using a plastic pipette, separate the two liquid phases; put the organic layer into a small beaker – YOU MUST DETERMINE WHICH LAYER HAS YOUR ORGANIC PRODUCT! Remember, you have an aqueous layer and an ether layer – what information do you need to look up to determine which layer is on the top and which is on the bottom? ***Never dispose of any layers until you have completed an experiment & have your product!**

7. To your organic layer, add a tiny (the very tip of a spatula!) amount of anhydrous powder to your organic layer in order to soak up any remaining water that you might have transferred over. Do NOT add a big scoop of anhydrous powder and soak up all the liquid – even the oily organic liquid; you will have to start over if you do!

8. Decant the liquid into another small clean beaker (not the powder).
9. GENTLY warm the beaker to evaporate off the ether. Do NOT heat on high – you will lose your oil product as it will burn and stick to the beaker. Just warm the beaker to evaporate off the ether, leaving an oil behind (your product).

10. Take an IR of your oil product (oils are nice because you can put a glove on and use your fingertip to smear the oil in the crystal trough instead of pouring such a tiny amount).

11. As always, analyze your IR in detail. All bonds and wavenumbers that are in your product should be labeled. The structure of your product should be on the IR too. Attach to lab.

12. Repeat the experiment until you have a pure product! You should no longer have the C=O bond at 1700cm^{-1}. What should you have?

12AL Prelab Experiment : "Pseudo" Grignard Reaction

1. Why would the glassware in a magnesium-based Grignard reaction need to be dried prior to performing the reaction? Explain clearly AND give a new example reaction to show what happens (example cannot be from this lab).

2. Draw the reagent below so that all of the charges actually show.

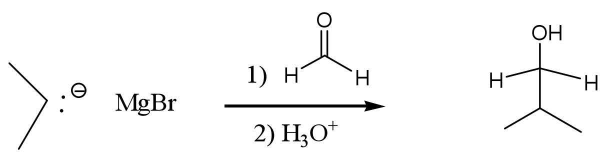
CH_3CH_2MgBr

3. Why is an aqueous solvent necessary for the second step of a magnesium-based Grignard reaction? Explain clearly AND give a new example reaction to show what happens (example cannot be from this lab).

4. Explain why Grignard reagents are extremely nucleophilic.

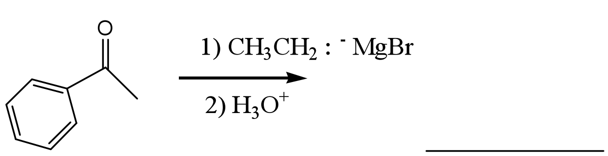
12AL Postlab Experiment : "Pseudo" Grignard Reaction

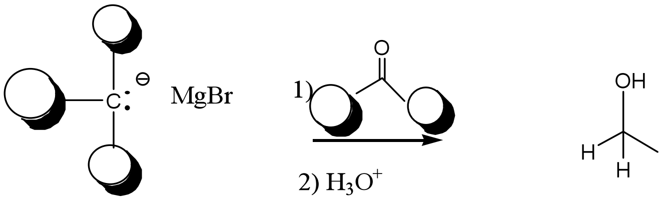
1. Draw the mechanism for the following reaction. All bonds, lone pairs, arrows, charges must be neatly & clearly shown.



2. Complete the blanks in the reaction sequences shown below.

3. Predict the product or reagents needed for the following reactions.





(Fill in the five circles. In other words, provide the grignard reagent and carbonyl structure that would be needed to make the product shown.)

4. Using a zinc-based Grignard reaction, show all the reagents/reactants/etc needed to synthesize the following product:

Tert-butoxide

5. Using a zinc-based Grignard reaction, show all the reagents/reactants/etc needed to synthesize the following product:

3-pentanol

6. Using a DIFFERENT zinc-based Grignard reaction, show all the reagents/reactants/etc needed to synthesize the same product in question 5:

3-pentanol